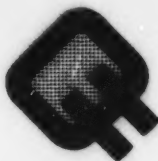


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EXECUTIVE SUMMARY

CYANIDE IN FLY ASH LEACHATES

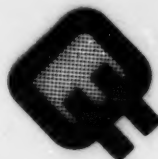
O. Herrmann

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There is a need to determine simple or weak-acid dissociable cyanide in fly ash leachates and wastewaters to ensure compliance with environmental standards. Total cyanide is considered to be less relevant environmentally because it includes strong complexes of cyanide in which the cyanide is much less available or reactive. For analysis of weak-acid dissociable cyanide, the cyanide is separated from the sample matrix as hydrogen cyanide by mild acidification and aeration of the sample. The hydrogen cyanide is trapped by passing the air stream through an alkaline solution. This technique is widely used and accepted. However, the final determination step generally used was considered to be undesirable because of the noxious or restricted reagents employed. A novel method was therefore developed which simply and rapidly converts cyanide to ammonia by oxidation with commercial bleach (sodium hypochlorite solution). The ammonia is then determined by the well-established phenate colorimetric method. A simple modification of an ammonia cartridge allows the oxidation and colorimetric determination to be carried out by an automated method. The detection limit is 0.04 mg cyanide /L.



job	file	date	report no.
740633-687-070	837.3	September 28, 1984	84-308-K



ontario hydro
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To Mr. F.J. Kee
Director of Research

CYANIDE IN FLY ASH LEACHATES

O. Herrmann

A new method has been developed for the determination of cyanide. The cyanide is separated from the initial sample (wastewater or fly ash leachate) by an accepted method which involves mild acidification and aeration of the sample and subsequent trapping of evolved hydrogen cyanide in sodium hydroxide. A novel continuous-flow analytical cartridge converts the cyanide to ammonia by oxidation with hypochlorite ion. The ammonia is then determined by colorimetry after color formation based on the phenate reaction. The detection limit is 0.04 mg cyanide /L. The relative precision is 2% at 0.2 mg/L.

1.0 INTRODUCTION

The Ontario Ministry of the Environment has established new guidelines for the allowable limits of cyanide (0.2 mg/L) in water and wastewaters. This limit is analytically defined in terms of weak acid-dissociable (WAD) cyanide. WAD cyanide is obtained by adjusting the pH of the sample (preserved at a pH>12 with sodium hydroxide) to 4 with sulfuric acid. This liberates hydrocyanic acid from simple cyanide and from some readily dissociated metal complexes such as those of cadmium and zinc. WAD cyanide therefore represents the readily available forms of cyanide. The liberated hydrocyanic acid or hydrogen cyanide (HCN) is separated from the bulk of the sample by sparging the sample with air and is collected in sodium hydroxide solution. This procedure separates WAD cyanide from less reactive forms of cyanide as well as from many other potential interferences in the sample. The use of strong concentrated acid would yield total cyanide (strictly speaking, total inorganic cyanide).

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The final determination step depends on the expected interferences and the convenience of the method. The most widely used methods appear to be colorimetric. The most frequently used of these methods involve reaction of cyanide with chloramine-T to form cyanogen chloride which is then reacted with pyridine-pyrazolone /1/ pyridine-p-phenylenediamine /2/ or pyridine-barbituric acid /3,4/ to form colored species. These methods suffer from the disadvantage that noxious or restricted reagents are required.

The cyanide ion-selective electrode, which provides an alternate method of determination, was not used for two reasons. The first of these was potential interference by chloride. High concentrations of chloride in the original sample, as found in some leachates, would result in the transfer of hydrogen chloride during the sparging stage. The second reason was the generally slow response of ion selective electrodes at low concentrations of analyte. Other potential methods such as gas chromatography (after derivatization) and liquid and ion chromatography were considered to be too troublesome and slow after an already slow initial separation.

The present work describes the development of a novel and simple continuous-flow colorimetric method which involves an easy modification of an existing system used for the determination of ammonia.

2.0 SEPARATION AND DETERMINATION OF CYANIDE

The separation of cyanide from many interferences by acidification of the sample to form hydrocyanic acid or hydrogen cyanide with subsequent removal by aeration is well established. Several similar types of apparatus are used (eg/ as in /3/). It was found that the flow rate of air through the system is crucial for quantitative recovery of cyanide. The optimum flow rate must be determined empirically for each system. Published values for "identical" systems should be used only as a starting point. The design of the trap was found to be critical. The inlet tube should pass as close to the bottom of the absorbing solution as possible in order to maximize the contact time between the gas stream and the solution.

An accepted reliable separation method was chosen with lesser emphasis on sample throughput because relatively few samples were expected initially. Available facilities presently limit the rate of sample separation to only 4-6 samples per day. Optimum economics and efficiency are therefore achieved by storing alkaline cyanide samples under refrigeration until a suitable batch size is obtained. A more rapid separation technique can be developed if sample numbers increase significantly. It was decided that a colorimetric method which could be adapted to continuous-flow techniques would be the most convenient final step for determining cyanide. A literature search failed to reveal any convenient methods for the formation of a colored species by direct reaction of cyanide. It was therefore decided to convert cyanide to a more convenient species.

Mild oxidation can convert cyanide to cyanate. In turn, cyanic acid (hydrogen cyanate) will decompose in acidic or mildly alkaline aqueous solution to form ammonia and carbonic acid (aqueous solution of carbon dioxide). Ammonia is a very convenient species for this laboratory to measure because a sensitive and convenient continuous-flow method for ammonia is already set up /5/.

Hydrogen peroxide was initially selected for evaluation as an oxidizing agent for cyanide because it works well in both alkaline and acidic media and the product of decomposition is water. Although it was found to work, the range of suitable concentrations was found to be too stringent for convenient operation. At low concentrations the conversion of cyanide was incomplete whereas at higher concentrations the excess peroxide interfered with the color forming reaction. Metallic oxidants were also rejected on the grounds of potential interference.

Hypochlorite ion was found to be a suitable oxidant. It readily oxidized cyanide and excess reagent did not pose a problem because this same reagent is used in the ammonia analysis system. Recovery of cyanide from fly ash leachate was tested by the standard addition technique. The samples were carried through the entire procedure in order to test both the separation method and the chemical conversion of cyanide to ammonia and its final determination. Results are shown in Table 1.

TABLE 1
RECOVERY OF CYANIDE

Sample	No	Cyanide Found (mg/L)	Recovery
A. Fly ash leachate	3	<0.04	N/A
B. A + 0.080 mg/L	3	0.084 ± 0.014	105 ± 16%
C. A + 0.250 mg/L	3	0.263 ± 0.010	105 ± 4%
D. A + 0.500 mg/L	3	0.528 ± 0.036	106 ± 8%

NOTE: ± values represent 2 sample standard deviations
N/A = not applicable

The relative precision of the method was found to be 1.9% at 0.2 mg/L and 1.3% at 4.0 mg/L based on 4 standards at each concentration.

Details of the method are provided in the Appendix.

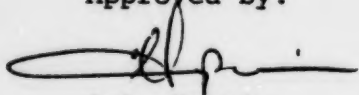
3.0 SUMMARY

A novel method has been developed which converts cyanide to ammonia by a simple reaction with hypochlorite ion. In combination with existing methods this allows the determination of cyanide in fly ash leachates and wastewaters at $\mu\text{g/L}$ concentrations.

4.0 ACKNOWLEDGEMENT

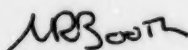
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5.0 REFERENCES

1. Epstein, J., Anal. Chem., 1947, 19, 272-274.
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3. Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, 1974, 40-47.
4. Standard Methods for the Examination of Water and Wastewater, 14th ed., American Public Health Association, 1975, 370-372.
5. R.E. Massey, Automated Ammonia Determination, Ontario Hydro Research Division Report No 80-414-H.

APPENDIX
DETERMINATION OF CYANIDE IN FLY ASH LEACHATES

1.0 Equipment and Supplies

- 1.1 Technicon Auto Analyzer IIC system with an ammonium cartridge and an additional reagent line and mixing coil.
- 1.2 Sufficient polystyrene sample cups (5 mL capacity) - 1 per sample plus 10-15 extra for blanks and standards.
- 1.3 Four 1L volumetric flasks
- 1.4 Sufficient 200 mL volumetric flasks- 1 per sample
- 1.5 Sufficient 100 mL volumetric flasks- 11 plus 1 per sample
- 1.6 A 1.5 L beaker
- 1.7 A 500 mL volumetric flask
- 1.8 A 100 mL pipette
- 1.9 An 8 mL pipette
- 1.10 Eppendorf pipettes ranging from 0.01 to 1.0 mL capacity
- 1.11 Distillation glassware consisting of inlet tube, 250 mL round-bottom flask, water-cooled condenser, connecting tubing and trap. Assemble as shown in Figure 1. (section 7.2) One set required per sample which is to be separated simultaneously.
- 1.12 Matheson #603 rotameter - 1 rotameter per 2 distillation sets.

2.0 Outline

The method is applicable to the determination of weak-acid dissociable (WAD) cyanide in fly ash leachates and wastewaters. The sample is filtered through a 0.45 μ m filter and is preserved with sodium hydroxide at a pH of at least 12.

When the sample is to be analyzed, the pH is adjusted to 4 (methyl orange indicator). "Simple" cyanide (presumably sodium cyanide) and weak complexes (such as those of cadmium and zinc) are converted to hydrogen cyanide which is stripped from solution by a stream of air. The hydrogen cyanide is trapped by passing the air through a bubbler containing 0.04 mole/L sodium hydroxide. This solution can be stored under refrigeration until enough samples have been processed to run a batch for determination.

The alkaline samples are diluted (to reduce the alkalinity) and oxidized with hypochlorite in a continuous-flow system to form cyanate. The cyanate hydrolyzes to ammonia and carbon dioxide. The ammonia is then determined by reaction with alkaline phenol and hypochlorite to form a colored species. The continuous-flow system is the same as that used for ammonia determinations except for the addition of an extra reagent line and mixing coil.

3.0 Interferences

The initial separation stage removes most potential interferences. Hydrogen halides and hydrogen sulfide are the only common species expected to be carried over at this stage although volatile organics may be present in some waste streams. Halides do not interfere. Sulfide and reducing organic species may

interfere. Ammonia would obviously interfere but would not normally be present because of the sample alkalinity.

4.0 Concentration Range

The concentration range is 0.04 to 2 mg/L when the high sensitivity colorimeter is used with the 50 mm x 2 mm flow cell. Samples with a higher concentration must be diluted.

5.0 Precision

The relative precision is about 8% at 0.04 mg/L and 2% at 0.20 mg/L.

6.0 Reagents

6.1 Alkaline Phenol

To a 1.5L beaker containing 50 mL deionized water, add 83g phenol and stir to dissolve. Cautiously add 180 mL sodium hydroxide (20% w/v) in small increments with continuous stirring. Dilute to 1L with deionized water and filter through glass fibre-C.

6.2 Complexing Reagent

To a 1.5L beaker containing 950 mL deionized water, add 33g potassium sodium tartrate and 24g sodium citrate and stir to dissolve. Adjust the pH to 5 with concentrated sulfuric acid. Dilute to 1L and add 1.5 mL Brij-35.

6.3 Sodium Hypochlorite (1 %)

Dilute 200 mL of household bleach containing 5.25% available hypochlorite to 1L with deionized water.

6.4 Sodium Hypochlorite (0.003 %)

Dilute 0.5 mL of household bleach to 1L with deionized water.

6.5 Sodium Nitroprusside

To a 1.5L beaker containing 900 mL deionized water, add 0.5g sodium nitroprusside. Stir to dissolve and dilute to 1L.

6.6 Sodium Hydroxide (1 mole/L)

To a 1L volumetric flask containing 600 mL deionized water add 40g sodium hydroxide. Stir to dissolve and make up to the mark.

- | | |
|--|--|
| 6.7 Sulfuric Acid (1+9) | Slowly add 100 mL concentrated sulfuric acid to 850 mL deionized water while stirring the solution. Cool to room temperature and dilute to 1L. |
| 6.8 Methyl Orange Indicator Solution | Dissolve 50 mg methyl orange in 100 mL deionized water. |
| 6.9 Stock Cyanide (1000 mg CN/L) | To a 1L volumetric flask containing 500 mL deionized water add 2.5029g of potassium cyanide. Swirl to dissolve and make up to the mark. Store at 4°C. |
| 6.10 Stock Cyanide (100 mg CN/L) | Dilute 100 mL of 1000 mg/L stock (6.9) to 1L in a volumetric flask with deionized water. |
| 6.11 Quality Assurance Stock (100 mg CN/L) | To a 1L volumetric flask containing 500 mL of deionized water add 0.25029g of potassium cyanide. Swirl to dissolve. Dilute to the mark and store at 4°C. |
| 6.12 Quality Assurance Standards (0.05 and 1.0 mg/L) | Add 0.1 and 2.0 mL of 6.11 to two 250 mL distillation flasks. Add 200.0 mL of deionized water to each flask with a pipette. Run in the same manner as samples. |

7.0 Procedure

7.1 Sampling and Storage

Samples are usually filtered through 0.45 μ m filters. The samples are preserved with sodium hydroxide at a pH no less than 12. Samples should be stored at 4°C.

7.2 Separation of Cyanide from Matrix.

7.2.1 The distillation apparatus is set up as shown in Figure 1. Add 8 mL of 1 mole/L sodium hydroxide to the gas washing bottle (the trap) and add 100 mL deionized water.

7.2.2 Adjust the vacuum so that air is being drawn into the aeration flask.

A water aspirator is a convenient vacuum source. If a pump is used, make sure that the suction is stable over long periods.

7.2.3 Bring the samples to room temperature.

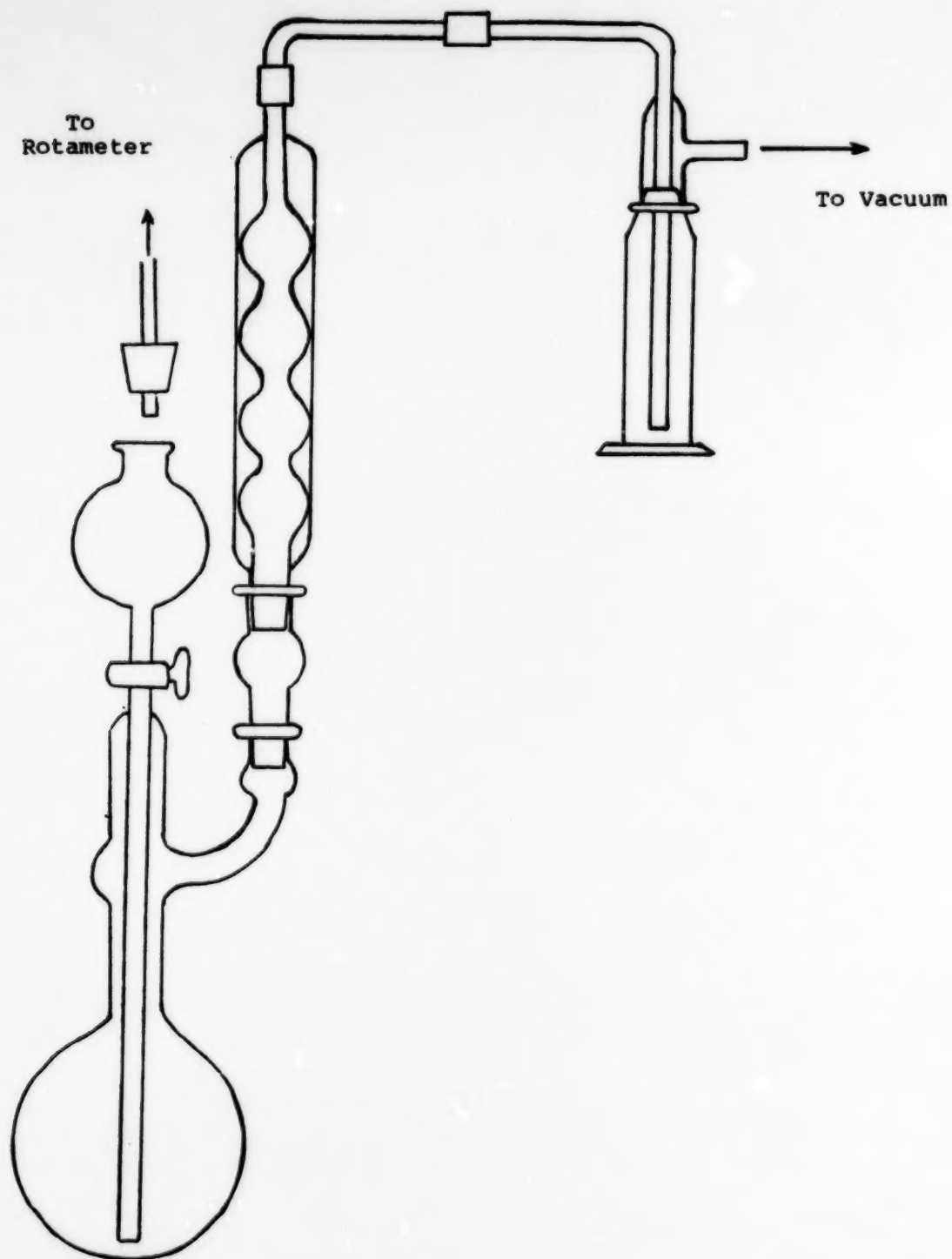


FIGURE 1
DISTILLATION APPARATUS

7.2.4 Add 3 drops of methyl orange indicator to the 250 mL flask through the thistle funnel. Add 200 mL of sample with a pipette through the funnel. Rinse the funnel with deionized water.

7.2.5 Add 1+9 sulfuric acid (6.7) dropwise until a definite color change to pink is observed.

7.2.6 Allow the air to pass through the sample at 2L/minute for 2 hours. Do not heat.

Check flow rate every 30 minutes.

7.2.7 Quantitatively transfer the solution from the absorption flask to a 200 mL volumetric flask. Make up to volume with deionized water.

Be sure to rinse the connecting tubes also.

7.2.8 Transfer a 25 mL aliquot of the solution from 7.2.9 to a 100 mL volumetric flask and dilute to the mark.

7.2.9 Process the high and low quality assurance standards in the same way as the regular samples above.

7.2.10 Run at least one duplicate sample for every ten samples if there is sufficient sample volume.

7.3 Preparation of standards

7.3.1 Add 1 mL of 1 mole/L sodium hydroxide to each of 10 deionized water rinsed 100 mL volumetric flasks.

7.3.2 Make 3 flasks up to volume with deionized water to serve as blanks.

7.3.3 Add 0.01, 0.05, 0.10, 0.25, 0.50, 1.00 and 2.00 mL of 100 mg/L cyanide stock to the other flasks and dilute to 100 mL.

This gives standards with 0.01, 0.05, 0.10, 0.25, 0.50, 1.00 and 2.00 mg CN per L.

7.4 Instrument Set-Up

7.4.1 The reagent lines and equipment should be assembled as shown in Figure 2.

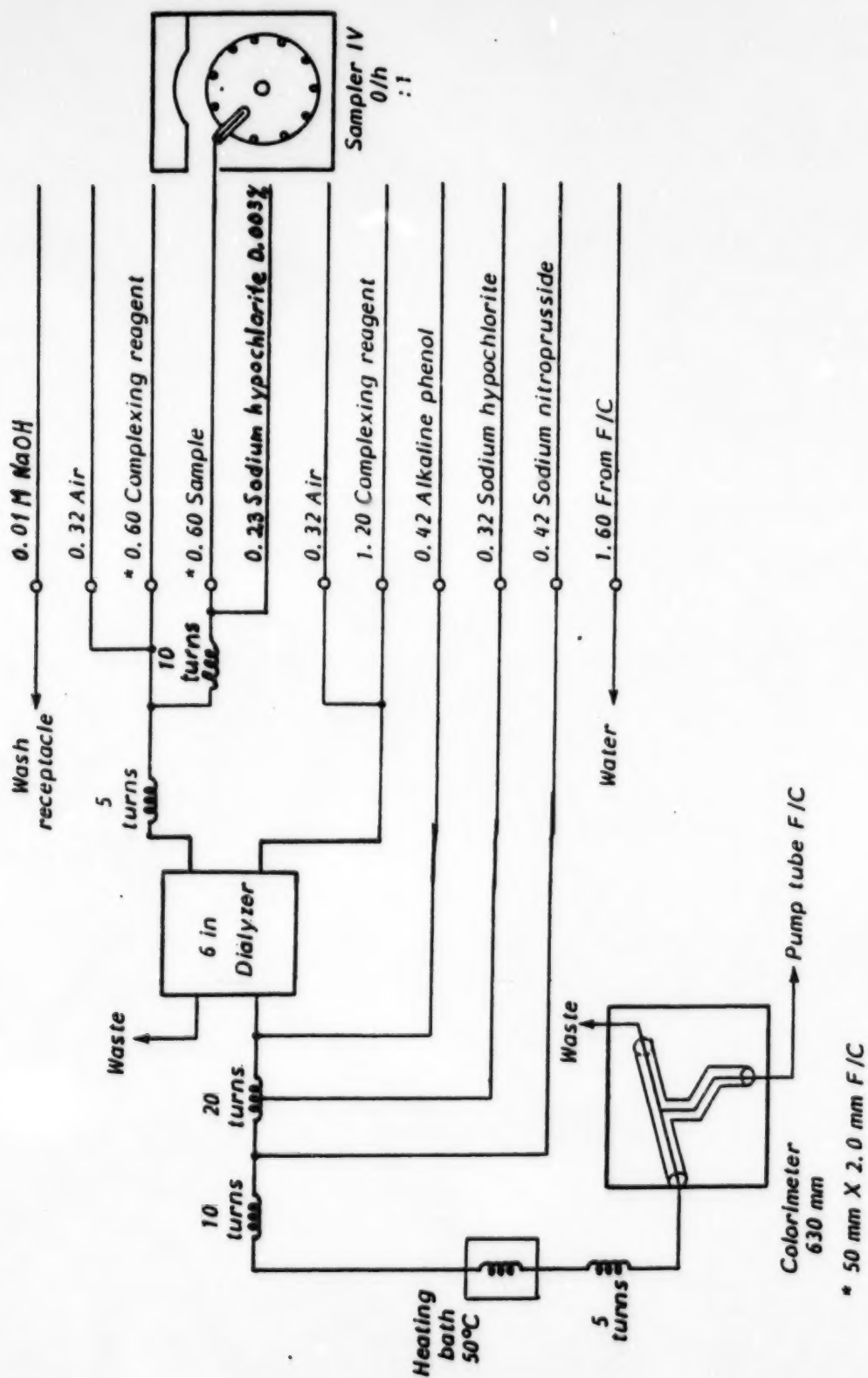


FIGURE 2
SCHEMATIC OF CONTINUOUS-FLOW ANALYZER FOR CYANIDE

7.4.2 Turn on the following:

(i)sampler (ii)pumps
(iii) colorimeter (iv)chart recorder (v)impact printer
(vi)data handler (vii)heater

Check to make sure there are sufficient reagents. Prepare any reagents required as described in section 6.0

7.4.3 Instrumental conditions:

-Wash solution- 0.01N NaOH
-Colorimeter- high sensitivity
-Flow cell- 50mm x 2mm ID
-Interference filter- 630 nm
-Chemistry type- Direct (D)
-Damping- normal
-Standard calibrate- Set highest standard to read 95 chart units. This is about a 6.4 setting for 2.0 mg CN/L.
-Samples / hour - 40
-Sample / wash ratio - 2:1
-Name of chemistry- Cyanide
-Calibration concentrations- 0.01, 0.05, 0.10, 0.25, 0.50, 1.00, 2.00 mg/L
-Calibration- linear

7.4.4 Set the tray protocol according to the number of samples as described in detail in section 1.7.4 of Research Report 82-521-K, Improved Dichotomous-Sampler Filter Analysis.

7.5 After the run is complete change the reagents to deionized water wash and wash for 30 minutes.

8.0 Calculations

8.1 The concentration of CN in the samples is given by:

$$\text{CN (mg/L)} = (a-b) * 4$$

where a= CN concentration in mg/L as given in the computer print-out.

b= average blank in mg/L

4= dilution factor during sample handling

8.2 Perform the same calculation on the quality assurance standards and enter the results in the log book.